

H₂ Evolution from Aqueous Solutions Containing Sacrificial Reagents with Photocatalytic Reaction

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Photocatalytic activity of metal loaded TiO₂ depends on characteristics of TiO₂ such as particle size, specific surface area and crystal structure etc. Photo catalytic activity for H₂ evolution of metal loaded TiO₂ was measured of decomposition of water containing methanol as sacrificial reagent under UV irradiation. In this reaction, H₂ evolution reached 16.9 ml/min using 2 wt% platinum loaded TiO₂ as a catalyst. Although when the same amount of ruthenium and rhodium loaded TiO₂ were used as a catalyst, H₂ evolution was only 2.7 and 4.5 ml/min. It was confirmed the transformation of the crystal structure of TiO₂ from anatase to rutile at room temperature in the deposition process of metals (Pt and Ru) on the surface of TiO₂ and the photo decomposition process of water with metal (Pt and Ru) loaded TiO₂, although the transformation is known to occur above 500 °C in ordinary circumstances.

Key words: Photocatalyst, Photodecomposition, Semiconductor

1. INTRODUCTION

The decomposition of water to H₂ and O₂ and the photogeneration of H₂ from water are attractive ways for the conversion of solar energy into chemical fuels. After discovery of Fujishima-Honda effect^{1, 2)}, the decomposition of water using semiconductor powders and layered compounds etc. were carried out^{3, 4)}. In this study we investigated the decomposition of water with semiconductor catalyst in the presence of alcohol as sacrificial reagent under UV light irradiation.

The photoactivity of TiO₂ catalyst is enhanced by metal loading such as Ru, Rh and Pt, because these metals can pool excited electron stably. It is well known that the catalyst's photoactivity is function of the particle size, surface area and crystal structure etc. In this study at one hand we have clarified characteristics of TiO₂ powders supplied by different manufacturers and at the other hand we have decomposed water efficiently.

2. EXPERIMENTAL

Seven kinds of TiO₂ powders were used as catalyst: Raremetallic-1, Raremetallic-2, P25, Tayca, Titankogyo, Kanto and Wako. RuCl₃, RhCl₃·3H₂O, PtCl₃ and RuCl₃·nH₂O were utilized as precursor to load metals on the surface of TiO₂. The load was carried out by a method similar to that of Kraeutler and Bard^{5, 6)}. TiO₂ powder (1.0g) was suspended in 100 ml of water including 1% ethanol and a calculated amount of RuCl₃, RhCl₃·3H₂O, PtCl₃ and RuCl₃·nH₂O solutions or suspension. The suspension was then irradiated with UV light by a 400W high pressure mercury lamp for 30 min. with magnetic stirring. Then, the grayish product was filtered with glass filter, washed several times with distilled water and dried at room temperature.

Photo reactions for water decomposition under the UV light irradiation were performed in a Pyrex reactor

with 350 ml of water containing 20 ml of methanol as a sacrificial reagent. The reactor was attached to an inner radiation type 400 W high pressure mercury lamp. The blank space of the reactor was filled by Ar gas to determine the produced gases.

Analysis

The volume of produced gases was measured by a gas buret and compositions were determined by a gas chromatograph (Shimazu; GC-8A molecular sieve 5A column, He carrier, TCD). The crystalline phases of the products were identified by X-ray diffraction analysis (Rigaku) using graphite-monochromatized Cu-K α radiation. The specific surface area was determined by the nitrogen gas adsorption method (Shibata SA-1000). Thermal properties of TiO₂ powders were measured with a Seiko Denshi model TG-DTA 220.

3. RESULTS AND DISCUSSION

Ru, Rh and Pt were loaded on the surface of TiO₂ from RuCl₃, RhCl₃ · 3H₂O and PtCl₃, respectively. RuCl₃ was used because when RuCl₃ · nH₂O was used as Ru metal precursor, the metal didn't deposit on TiO₂ surface. 2 wt% of Ru, Rh and Pt was loaded on the surface of Raremetallic-2 TiO₂ respectively to compare catalytic activity. The gas

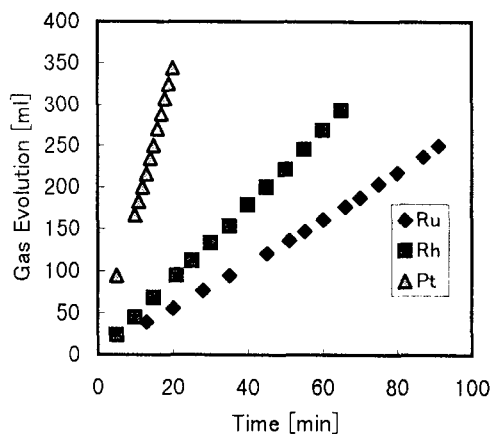


Fig.1 Photo catalytic activity of 2 wt% metals loaded TiO₂ (Raremetallic-2)

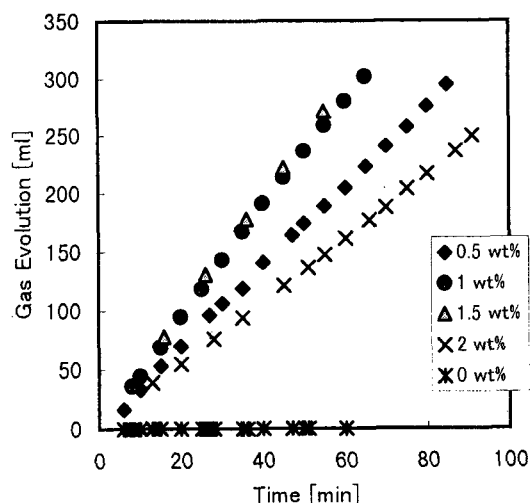


Fig.2 Photo catalytic activity of TiO₂ (Raremetallic-2) with different amounts of Ru

evolution with photo reaction using Ru, Rh and Pt loaded TiO₂ as catalyst were 2.7, 4.5 and 16.9 ml/min respectively (Fig.1).

0.5, 1, 1.5 and 2 wt% of Ru were loaded on Raremetallic-2 TiO₂ and the photo activity was compared as shown in Fig.2. The photo catalytic activity of 1 and 1.5 wt% loaded TiO₂ was better than that of 0.5 wt%. However, when the 2 wt% Ru loaded TiO₂ was used, the activity decreased remarkably. It indicates that excess load of Ru on TiO₂ disturbs the absorption of

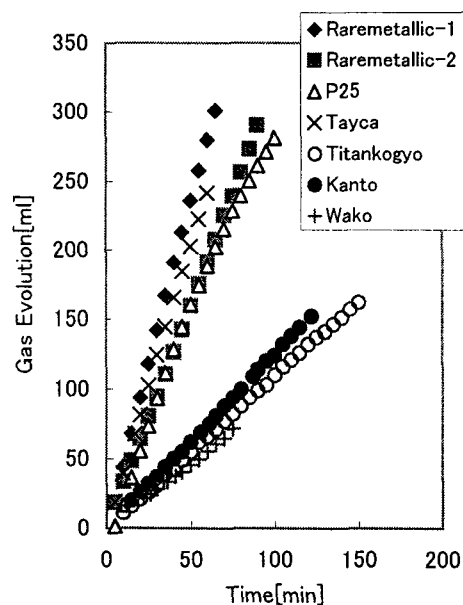


Fig.3 Photo catalytic activity of 1 wt% Ru loaded TiO₂

Table I Characteristics of TiO₂

TiO ₂	Crystallinity	Crystal Structure	Specific Surface Area [m ² /g]	Gas Evolution [ml/min]
Raremetallic-1	○	Anatase	—	4.7
Raremetallic-2	○	Anatase	12.5	3.2
P25	△	Anatase, Rutile	42.3	3.0
Tayca	△	Anatase	47.5	4.1
Titankogyo	△	Anatase	54.3	1.1
Kanto	◎	Anatase	7.96	1.3
Wako	◎	Anatase	8.45	0.9

The photo reaction carried out under UV region with 400W high pressure mercury lamp under existence of sacrificial reagent (CH₃OH).

light energy for charge separation.

Fig.3 shows the gas evolution from aqueous solution containing methanol using 1 wt% Ru loaded TiO₂ catalysts supplied by different manufacturers. Photo activity of these catalysts depends on the crystal structure, surface area and crystallinity etc. Table I shows the characteristics of these TiO₂ powders. It is well known that TiO₂ works better as catalyst in the anatase crystal structure: All tested TiO₂ powders have pure anatase crystal structure except the P25 which has mixed structure of anatase and rutile.

We have confirmed the change of structure of TiO₂ from anatase to rutile in the deposition process of Ru and Pt metals and the photo reaction process with Ru and Pt loaded TiO₂ used as catalyst (Fig.4). Similar phenomenon was reported by Yanagisawa et al⁷⁾. In that case, they used TiO₂ intercalated H₄Nb₆O₁₇ catalyst for water decomposition. In general, TiO₂ transforms its structure from anatase into rutile in a thermal treatment above 500 °C, but they confirmed the change in the process of TiO₂ sol intercalation to the layer of H₄Nb₆O₁₇ at 60 °C under UV irradiation. Our study and their results of unusual rutile formation allow us to consider that H₄Nb₆O₁₇ and metals (Ru, Pt) loaded on the surface of TiO₂ act as nuclei to form rutile.

Although the high photo activity of P25 is well known, in this study we confirmed high photocatalytic activity of Raremetallic-1 TiO₂ as catalyst for H₂

evolution under UV irradiation. During long time reaction the photo catalytic activity of P25 and Titankogyo TiO₂ decreased. In these cases, H₂ evolution is not linear to the reaction time and it is influenced by the size of the particles. The decrease of the activity may be explained by the transformation of anatase to rutile which shows lower activity, but this hypothesis could not be confirmed clearly by XRD patterns.

On the other hand, Titankogyo TiO₂ doesn't have high activity as photo catalyst although it has the largest

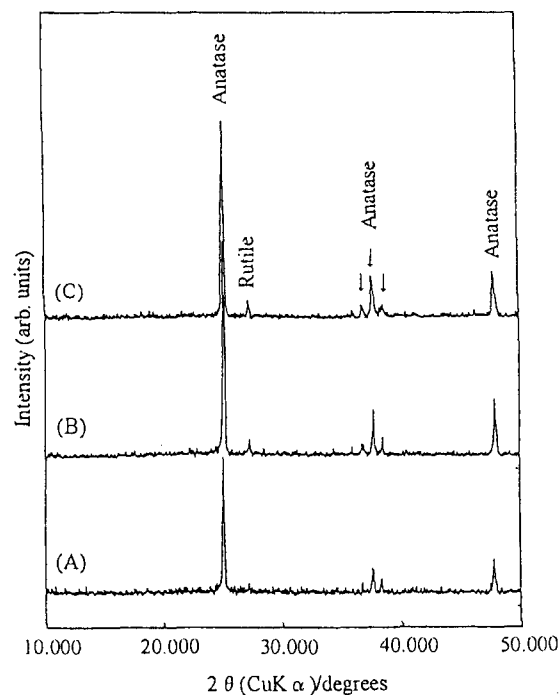


Fig.4 XRD patterns of (A) TiO₂ (Raremetallic-2), (B) after the photo reaction of 2 wt% Ru loaded TiO₂ (Raremetallic-2) and (C) after the photo reaction of 2 wt% Pt loaded TiO₂ (Raremetallic-2)

specific surface area as 54.3 m²/g in these TiO₂ powders. We considered that Titankogyo TiO₂ contains organics as impurities in the production process because when the Titankogyo TiO₂ was calcined at 200 °C for 2 hr in air, the color changed from white to brown indicating the presence of carbonization reaction. It was observed two step decreases of Titankogyo TiO₂ weight by TG measurement from 20 to 600 °C. The weight loss observed at 20-80 °C (-0.6%) corresponded to loss of absorbed water on the Titankogyo TiO₂ surface and the weight loss observed at 280-600 °C (-1.8%) might correspond to loss of organic impurity. The impurities might disturb the photocatalytic reaction.

We tried to decompose water with unloaded TiO₂ in the presence of methanol as sacrificial reagent in UV light irradiation, but we couldn't confirm any gas evolution.

4. CONCLUSIONS

Ru, Rh and Pt were loaded on TiO₂ from RuCl₃, RhCl₃·3H₂O and PtCl₃. Metals loaded on TiO₂ powders enhanced photo catalytic activity, and we observed the highest gas evolution as 16.9 ml/min with 2 wt% Pt loaded TiO₂ (Raremetallic-1) catalyst in this study. In these photo catalytic reactions, the gas evolution continued for more than 4 hrs. However the decreases of gas evolution per unit time was observed when Pt loaded TiO₂ (Raremetallic-2) or Ru loaded TiO₂ (P25) was used as a catalyst. In these cases, we confirmed the transformation of the structure of TiO₂ from anatase to rutile. This is probably the reason of decrease of photo catalytic activity. To avoid such transformation reaction of TiO₂ under mild conditions should be important.

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